

Radiation Resistant Polypropylene Useful in Medical Applications

Field of the Invention

This invention relates to the development of an improved clear, color-stable, and radiation-sterilizable polypropylene for various medical applications, including syringes and other wares normally fabricated from what is recognized in the art as radiation-sterilizable polyolefins.

Background Information

US patent 4,666,959 teaches the use of a polymeric hindered amine light stabilizer, an alkyl phosphite and a specific phenolic antioxidant as necessary additives to protect polypropylenes from the exposure to high energy "gamma" radiation. US patent 4,888,369 teaches very similar art as the previous one, except it teaches the use of an additive termed as mobilizer, such as hydrocarbon oil. Although the teachings of these patents are helpful to prevent degradation of polypropylenes from exposure to high energy radiation, the main drawbacks are the yellowing of parts made from the teachings therein due to the presence of hindered phenolic antioxidants. US Patent 6,231,936 claims the radiation tolerant polypropylene composition comprising of polypropylene and polyethylene (1-50%) produced by single-site catalyst along with additives such as hindered amine stabilizers, secondary antioxidants (i.e., phosphites and thioesters), sorbitol type clarifiers. However secondary antioxidants such as phosphites are susceptible to hydrolysis upon exposure to moisture prior to or during extrusion. Also,

in the real world case scenario, most of these phosphites are recognized by those skilled in the art as being the cause of black specks in the resin which show up in the molded parts thereafter. This patent also claims the use of thiodipropionate secondary antioxidant selected from the group consisting of distearyl thiopropionate and dilaurylthiopropionate. These sulfur containing additives are known to impart odor. This patent also claims the addition of a sorbitol type clarifying agent (i.e., bis-4-methylbenzylidene sorbitol and bis-3,4-dimethylbenzylidene sorbitol) up to 0.5% to enhance clarity of molded parts. However, sorbitol type clarifying agents impart cherry flavored odor, and in some severe autoclave conditions (per 9 CFR 121 condition A), they form flocculates. US patent 5,376,716 describes a radiation resistant resin suitable for the manufacture of disposable medical devices comprising of a semicrystalline polypropylene or propylene-ethylene copolymer with 1500 - 5000 ppm of triallyl trimellitate as well as a phosphite.

The presentation "New Improvements in Radiation Resistant Polypropylenes" presented at the Fifth International Conference Additives in 1996 showed the formulations consisting of special additives combinations of hindered amine light stabilizers ("HALS") and phosphites improved the color-stability of polypropylenes after exposure to gamma radiation.

The polypropylenes commonly contain a hindered phenolic antioxidant along with a secondary antioxidants such phosphites and thioesters as the processing stabilizers. However, upon exposure to gamma radiation, it exhibits undesirable color due to generation of color-bodies from the oxidized hindered phenolic type primary antioxidants. A non-hindered phenolic additive system for such applications is

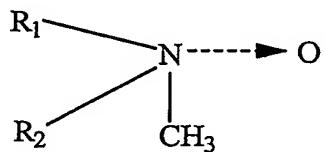
desired. Although addition of a phosphite prevents the discoloration, the phosphite is also the main source of causing black specks in the products during the end-use applications. Although thioesters are good processing as well as thermal stabilizers, they do impart odor, which is not acceptable for most medical uses. Hence, this invention relates to an additive composition that is free of both hindered phenolics, and secondary antioxidants such as phosphites and thioesters. It comprises a combination of a hindered amine light stabilizer and an amine oxide, or a combination of hindered amine light stabilizer and hydroxyl amine compounds that provided excellent color stability after exposure to gamma radiation up to 5 mrads. Also addition of clarifier such as NA-21 (Amfine Chemical Corporation) imparted excellent clarity.

The present invention remedies the aforementioned deficiencies by achieving better color stability along with enhanced clarity and impact resistance. A polypropylene random copolymer (nominal MFRs and 9 and ~ 25 dg/min @ 230C/2.16kg per ASTM D-1238) consisting of: I) a combination of hindered amine light stabilizer ("HALS") and an amine oxide along with an acid neutralizer (i.e., metallic stearate) or II) a combination of HALS and hydroxyl amine along with an acid neutralizer was exposed to gamma radiation up to 5 mrads. The results indicated that HALS/amine oxide or HALS/ hydroxylamine maintained excellent color stability, even showing very little increase in yellowness index after exposure to gamma radiation. Addition of a new clarifier NA-21(Amfine, Allendale, NJ) imparted better clarity having less effect on tensile and impact properties unlike sorbitol based clarifier such as MILLAD® 3988 (Milliken Chemical Co, Spartanburg, South

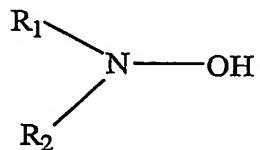
Carolina). Addition of a metallocene catalyzed polyethylene polymer and Ziegler-Natta catalyzed polyethylene containing octene as a comonomer improved the impact strength of the polymer after being exposed to gamma radiation.

Summary of the Invention

The present invention provides a blend useful as an additive in polyolefin polymers for minimizing the effects of radiation on the physical properties of said polymers, which comprises a hindered amine light stabilizer and at least one material selected from the group consisting of: i) amine oxides exemplified by the formula:



in which R_1 and R_2 are each independently selected from C_{10} to C_{24} alkyl, aryl, or alkylaryl groups, whether straight-chain, branched, cyclic, saturated, or unsaturated; and ii) hydroxylamines exemplified by the formula:



in which R_1 and R_2 are each independently selected from C_{10} to C_{24} alkyl, aryl, or alkylaryl groups, whether straight-chain, branched, cyclic, saturated, or unsaturated.

Detailed Description

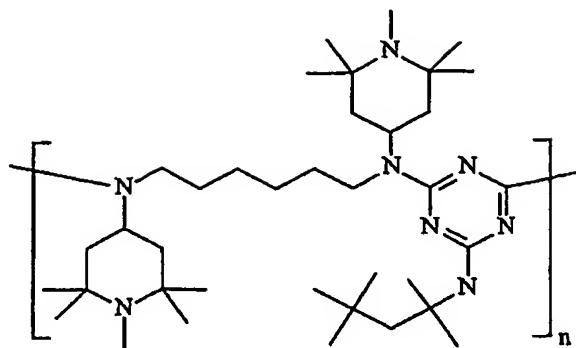
Semi-crystalline polymers such as polypropylene are used in medical devices, and food packaging where these articles are frequently subjected to ionizing radiation for sterilization. It is known that exposure of polymers such as polypropylene to high-energy radiation i.e., electron beam or gamma radiation triggers radiation induced chemical reactions with predominant chain scission mechanism, resulting in loss of physical properties. Such property losses include embrittlement and discoloration, and are not acceptable to end-use applications.

The present invention provides novel formulations of polypropylene compositions that are radiation resistant, color-stable and clear. In accordance with the present invention, polypropylene and propylene-ethylene copolymer compositions comprise of the following components in amounts equal to about: i) 0.01 - 0.2 wt% hindered amine light stabilizer ("HALS"); ii) 0.01 - 0.1 wt% amine oxide; iii) 0.01 - 0.2 wt% hydroxyl amine; iv) 0.01 - 0.3 wt% clarifier or nucleator; and v) 0.01 - 0.2 wt% acid neutralizer. The general chemical formulae for amine oxides and hydroxyl amines are illustrated as:



Hydroxyl Amine (IRGASTAB® FS-042)
(Ciba Specialty Chemicals)

Amine Oxide (GENOX® EP)
(Crompton Corporation)



Hindered Amine Light Stabilizer, CHIMASSORB® 944, (Ciba Specialty Chemicals)

A combination (1:2) of amine oxide (GENOX® EP) and HALS or 1:1 blend of hydroxyl amine (FS-042) with HALS (CHIMASSORB® 944) more commonly known as IRGASTAB® FS 410 were thoroughly tested, and compared to those of prior art. Individual additives in various radiation-resistant formulations include: Naugard XL-1 (CAS #70331-94-1, 2,2'-oxiamidobisethyl 3(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, Crompton Corporation); TINUVIN® 622LD (CAS #65447-77-0, Dimethyl succinate polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol; Ciba Specialty Chemicals); CHIMASSORB® 944LD (CAS #71878-19-8;N, N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine polymer with 2,4,6-trichloro-1,3,5-triazine and 2,2,4-trimethyl-1,2-pentaamine, Ciba Specialty Chemicals); GENOX® EP (CAS #204933-93-7; Dialkyl methyl amine oxide; Crompton Corporation); IRGASTAB ® FS410 (1:1 blend of IRGASTAB® FS042 and CHIMASSORB® 944LD from Ciba Specialty Chemicals); DHT-4A (CAS # 11097-59-9; Synthetic hydrotalcite; Kyowa Chemical); Calcium Stearate (CAS # 1592-23-0;Crompton Corporation); PEP-36 (CAS #80693-00-1;Bis (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol-di-phosphite; Amfine Chemical)

ULTRANOX® 641 (CAS #161717-32-4; 2,4,6-tri-tert-butylphenyl 2, butyl 2ethyl 1,3prpane diol phosphite; Crompton Corporation); and WESTON® 619 (CAS #3806-34-6, Distearyl Pentaerythritol Diphosphite; Crompton Corporation).

Additives useful for improving clarity and nucleation in polyolefin polymers include: MILLAD® 3988 (CAS # 135861-56-1; Bis 3,4,-dimethylbenzylidene sorbitol, from Milliken Chemical); HPN-68 (CAS # 351870-33-2, Proprietary inorganic salt from Milliken Chemical); NA-21 (Proprietary inorganic salt from Amfine Chemical); NA-11 (CAS #85209-91-2, Sodium 2,2'-methylene-bis-(4,6-di-tert-butylphenyl)phosphate; from Amfine Chemical); and KM-1500 (CAS #1309-43-4 and 68440-56-2; Magnesium Salt of disproportionated rosin acid; Mitsui&Co).

Impact Modifier additives useful for improving impact properties in polyolefin polymers include: ENGAGE® 8200 polyethylene (CAS #026221-73-8); DuPont Dow Chemical); Catalyst LL-1002.09 (CAS #25087-34-7, Ziegler-Natta Catalyzed Linear Low Density polyethylene with butene comonomer; ExxonMobil Chemicals); and Catalyst L8101 (CAS #26221-73-8, Ziegler-Natta Catalyzed Linear Low density polyethylene with octene comonomer; Huntsman Polymers Corporation, Odessa, Texas.)

An unexpected result of the invention includes improved color stability, enhanced clarity, and improved impact resistance after being exposed to gamma radiation without use of conventional phosphite and thioesters. The present invention is exemplified by what is contained in the examples now presented, and shall not be construed as being limited thereby in any fashion.

Example 1

The formulations A1 through N1 are given in Tables 1 and 2. Several formulations had hindered amine light stabilizer (HALS)/phosphites. The phosphites used are ULTRANOX® 641 phosphite (Crompton Corporation, Middlebury, CT), WESTON® 619 phosphite (Crompton Corporation, Middlebury, CT), DOVERPHOS® S-9228T phosphite (Dover Chemical, Dover, OH), PEP-36 (Amfine, Allendale, NJ). Also, clarifiers/nucleators such as MILLAD® 3988 (Milliken Chemical Spartanburg, SC, HPN-68 (Milliken Chemical, Spartanburg, SC), NA-21 (Amfine Chemical, Allendale, NJ), and KM1500 (Mitsui Chemical) were added at specified levels. The hindered amine light stabilizers are TINUVIN® 622 HALS and CHIMASSORB® 944 HALS (Ciba Specialty Chemicals, Tarrytown, NY). The amine oxide is GENOX® EP amine oxide (Crompton Corporation, Middlebury, CT.). The impact modifier chosen was ENGAGE® 8200 polyethylene (DuPont-Dow). The specific formulations were pre-blended with un-stabilized polypropylene random copolymer powder (MFR ~ 12 g/10min), and then melt extruded by a Haake TW100 twin screw extruder at a processing temperature of 230°C. Test specimens were molded on a 120-ton Van Dorn injection-molding machine under ASTM Conditions. Specimens were irradiated at 2.0 and 4.0 mrads by Isomedix, Whippny, NJ using a ⁶⁰Co source. Control specimens (i.e., non-radiated) were included in each physical test for comparison. Yellowness Index was measured with a Colorgard/05 from BYK Gardner as per ASTM D-1925. Tensile properties were measured on Typ1-I injection molded tensile bars with an Instron 1125 universal testing machine with an initial grip separation of 2.5" and an extension rate of 5"/min. Melt flow rate (MFR) was

measured with a Kayness Galaxy I melt indexer as per ASTM-1238B. Multiaxial impact energy was measured by Dynatup 8250, using velocity of 4.3m/sec and crosshead weight of 28 lbs (12.7kg).

Effect of Gamma Radiation on MFR: The % change in MFR after exposing the samples at 2 and 4 mrads are given in tables 1 and 2. Sample K1 (containing CHIMASSORB® 944 @ 0.15% and ULTRANOX® 641 @ 0.1%) had the least increase of 316.7% in MFR after 2 mrads of exposure, whereas sample F1 (control - containing 0.2% TINUVIN® 622 + 0.1% WESTON® 619) had the highest increase of 671.7%. At 4.0 mrads of exposure, sample M1 (0.15% CHIMASSORB® 944+0.1% PEP-36 + 2.5% ENGAGE® 8200) had the least increase of MFR, whereas Sample F1 (Control sample) had the highest increase in MFR of 1704.3%. Sample J1 (containing CHIMASSORB® 944 @ 0.1%, and GENOX® EP @ 0.05%) had the corresponding increase of 325% and 741.7% at 2.0 and 4.0 mrads of exposure, showing that it was relatively more stable compared to the control sample F1.

In all tables herein, all amounts given in formulations are specified in percentages on a weight basis, based on the total weight of the compositions provided.

Table I							
Sample ID	A1	B1	C1	D1	E1	F1	G1
PP Powder (MFR ~10 dg/min)	99.575	99.525	99.495	99.425	99.495	99.23	99.475
CHIMASSORB® 944	0.15	0.15	0.15	0.15	0.15		0.15
TINUVIN® 622						0.2	
ULTRANOX® 641	0.1	0.1	0.1	0.1	0.1		0.1
DOVERPHOS® S-9228T							
Genox EP							
Calcium Stearate	0.05	0.05	0.05	0.05	0.05	0.1	0.05
DHT-4A	0.025	0.025	0.025	0.025	0.025	0.05	0.025
Naugard XL-1						0.07	
Weston 619						0.1	
NA-21	0.1	0.15	0.18	0.1			
Millad 3988				0.15	0.18	0.25	0.15
NA-11							0.05
Physical Properties at 0.0 Mrads							
MFR (g/10min)	12	11	11	11	11	9.2	12
% Strain at Yield	13.5	13.6	13.9	14	13.9	12.4	14.1
Stress at Yield, psi	4200	4220	4220	4270	4350	4570	4340
% Strain at Break	560	580	570	610	660	650	650
Stress at Break, psi	2760	2770	2780	2770	2850	2910	2860
Multiaxial Impact @ 23°C,in-lbs	250(112)	278(114)	254(73)	52(29)	27(13)	21(4)	157(84)
Yellowness Index	4.5	4	3.9	4.6	4.8	4.2	4.8
% Haze-25mil	8.5	7.8	7.3	8.3	8.6	10.7	9.1
% Haze-50mil	23.2	21.6	20.7	22.5	21	22.6	21.1
Crystallization Temp (°C)	118.3	119.6	119.4	119.7	119.9	120.9	121
at 2.0 Mrads							
MFR (g/10min)	51	55	56	63	59	71	55
% Strain at Yield	13.6	13.7	13.7	14.1	13.8	11.9	14
Stress at Yield, psi	4170	4190	4190	4230	4320	4570	4350
% Strain at Break	630	620	620	440	510	340	570
Stress at Break, psi	2720	2740	2730	2670	2760	2620	2770
Multiaxial Impact @ 23°C,in-lbs	111	167	131	24	27	22	93
Yellowness Index	4.6	4.4	4.5	5.2	5.8	6.2	6.5
4.0Mrads							
MFR (g/10min)	147	118	129	113	127	166	137
% Strain at Yield	14.4	14	14.2	13.6	14.2	13.1	13.9
Stress at Yield, psi	4150	4200	4190	4330	4470	4590	4400
%Strain at Break	690	660	640	330	340	170	270
Stress at Break, psi	2720	2690	2690	2640	2670	3410	2690
Multiaxial Impact @ 23°C,in-lbs	55	85	43	18	15	15	35
Yellowness Index	5.4	4.8	5.4	5.7	7	6.5	7
%Change in MFR (@ 2 Mrads)	325	400	409.1	472.7	436.4	671.7	358.3
%Change in MFR (@ 4 Mrads)	1125	972.7	1072.7	927.3	1054.5	1054.5	883.3
Diff. In YI (2.0-0 Mrads)	0.1	0.4	0.6	0.6	1	2	1.7
Diff. In YI (4.0-0 Mrads)	0.9	0.8	1.5	1.1	2.2	2.3	2.2

Effect of Nucleator/Clarifiers: Since, gamma radiation on clarity of PP has negligible effect, the step-plaques (25/50 mils) were not subjected to gamma radiation. The % haze (for 25 mil plaque) of samples A1, B1, and C1 (containing NA-21 @ 0.1,

0.15, and 0.18% respectively) were 8.5, 7.8, and 7.3 respectively, showing very excellent enhancement in clarity. The corresponding % haze for 50 mil plaques were 23.2, 21.6, and 20.7 respectively, showing excellent clarity. The percentage of haze in samples E1 and L1 (Duplicate run - both containing Millad 3988 @ 0.18%) were 8.6 and 6.3 respectively; showing some variability. However, this might be attributed to the dispersion of MILLAD® 3988 (i.e., poor dispersion may cause higher % haze). Hence in a reactor grade PP, both NA-21 and MILLAD® 3988 imparted similar enhancement in clarity (i.e., reduction in %haze). Samples M1 and N1 (containing 2.5% and 5% ENGAGE® 8200) had the %haze (25 mil) of 8.2 and 9.3 respectively. This indicated that the modifier (i.e., ENGAGE® 8200) had very little effect on clarity. Combination of MILLAD® 3988/HPN-68 (@ 0.15%/0.05%) in samples H1, J1 and I1 imparted % haze values of 9.2, 7.4, and 7.5 units, measured on 25 mil thick plaques. Also, these three samples had crystallization temperatures almost 2° higher than that of sample C1 (containing NA-21 @ 0.18%). Higher crystallization temperature normally results in lower cycle time, and higher productivity.

Effect of Gamma Radiation on Yellowness Index: The initial colors of samples A1 through N1 were in the range of 2.1 – 5.4 units. Sample H1 had the highest initial color of 5.4. The control sample F1 had the initial color of 4.2 units, 6.2 units @ 2 mrads, and 6.5 units @ 4 mrads, thus an increasing trend in yellowness index with increase of dosage of gamma radiation. Sample I1 (0.15% C-944+ 0.1% DOVERPHOS® S-9228T) had initial color of 4.3 @ 0.0 mrads, 3.9 units @ 2.0 mrads, and 3.9 units @ 4.0 mrads, thus showing slight decrease in yellowness index with increase in dosage of gamma radiation. Sample J1 (0.1% C-944+0.05%

GENOX® EP had initial color of 4.6 units, 2.3 units @ 2 mrads, and 2.6 units @ 4 mrads, thus showing decrease in yellowness index with increase in dosage of gamma radiation. All other formulations showed an increase in yellowness index with increase of the dosage of gamma radiation.

Table 2							
Sample ID	H1	I1	J1	K1	L1	M1	N1
PP Powder	99.475	99.475	99.575	99.475	99.495	99.875	99.375
CHIMASORB 944	0.15	0.15	0.15	0.15	0.15	0.15	0.15
TINUVIN 622							
ULTRANOX 641	0.1	-	-	0.01	0.01	0.01	0.01
DOVERPHOS-9228T	-	0.01	-	-	-	-	-
GENOX EP	-	-	0.05	-	-	-	-
Ca stearate	0.05	0.05	0.05	0.05	0.05	0.05	0.05
DHT-4A	0.025	0.025	0.025	0.025	0.025	0.025	0.025
MILLAD 3988	0.15	0.15	0.15	0.15	0.18	0.15	0.15
HPN-68	0.05	0.05	0.05	-	-	0.05	0.05
KM-1500	-	-	-	0.05	-	-	-
PEP-36	-	-	-	-	-	0.1	0.1
EXXACT 8200	-	-	-	-	-	2.5	5
Physical Properties of Samples from above at 0 megarads							
Sample	H1	I1	J1	K1	L1	M1	N1
MFR	12	12	12	12	12	11	12
% strain @ yield	14.3	14.2	14.2	14.3	3.9	14.9	15.4
Stress @ yield (psi)	4290	4250	4260	4320	4360	4020	3880
% strain @ break	630	610	620	620	700	590	630
Stress @ Break (psi)	2790	2800	2810	2820	2850	2750	2740
multiaxial impact @ 23°C, in-lbs	257	301	285	278	318	334	325
yellowness index	5.4	4.3	4.6	4.6	5.9	3.7	2.1
% haze 25mil	9.2	7.4	7.5	8.1	6.3	8.2	9.3
%haze 50mil	21.6	19.6	18.9	20.5	14.3	20.6	23.7
crystallization temp.	121.5	122.5	122.5	120.1	120.9	121.9	122
at 2.0 megarads							
MFR (g/10min)	58	62	51	50	54	47	57
%strain@yield	14.2	14.2	14.2	13.8	14.1	14.5	15.3
stress@yield, psi	4280	4260	4280	43410	4400	4080	3880
%strain@break	480	320	640	530	670	580	580
stress@break (psi)	2700	2680	2800	2770	2870	2720	2690
multiaxial impact @23°C, in-lbs	131	106	201	160	155	291	307
yellowness index	6.9	3.9	2.3	4.7	5.1	6.7	5.7
at 4.0 megarads							
MFR (g/10min)	118	107	101	129	116	91	117
%strain@yield	13.6	14	14.3	13.7	14	14.5	15.1
stress@yield, psi	4300	4290	4270	4320	4380	4060	3880
%strain@break	280	270	290	300	340	370	570
stress@break (psi)	2670	2640	2640	2650	2690	2610	2610
multiaxial impact @ 23°C, in-lbs	58	45	37	50	31	243	294
yellowness index	7.7	3.9	2.6	6	6.2	5.1	4.5
% in MFR @ 2.0 megarads	383.3	416.7	326	316.7	350	327.3	375
% in MFR @ 4.0 megarads	883.3	791.7	741.7	975	866.7	727.3	875
in YI (0-2.0 megarads)	1.5	-0.4	-2.3	0.1	-0.8	3	3.6
in YI (2.0-4.0 megarads)	2.3	-0.4	-2	1.4	0.3	1.4	2.4

Effect of Gamma Radiation on Tensile Properties: % Strain @ yield was unaffected by increase in dosage of gamma radiation. % Strain @ break was affected to some degree with increase in dosage of gamma radiation. At 2.0 mrads of exposure, the losses in % strain at break of various formulations were in the range of 1.7% - 47.5%; Sample F1 had the highest loss of % strain at break. M1 (containing 2.5% ENGAGE® 8200) had 1.7% loss of strain at break at 2.0 mrads and 37.3% loss at 4mrads of exposure respectively. Sample N1 (containing 5% ENGAGE® 8200) had the corresponding loss of 7.9% and 9.5% at 2 and 4 mrads respectively. Hence, it is evident that addition of ENGAGE® 8200 (@ 2.5 – 5%) helped to maintain the % strain at break.

Effect of Gamma Radiation on Multiaxial Impact: Multi-axial impact of samples A1 through N1 were measured by 8250 Dynatup with an impact of 26 lbs under acceleration due to gravity. The initial impact values varied from 21 in-lbs to 334 in-lbs. It was evident that the samples containing MILLAD® 3988 had the least impact values compared to the samples containing NA-21. The loss of impact at 2 mrads were in the range of 0 – 55.6%. The loss of impact at 4 mrads were in the range of 9.5 – 89.4%, showing a higher degree of loss at this dosage of gamma radiation. Sample M1 (containing 2.5% ENGAGE® 8200) had a loss of ~27% in impact; whereas sample N1 (containing 5% ENGAGE® 8200) had only 9.5% loss of impact. Hence, it is evident that addition of ENGAGE® 8200 helped to maintain impact properties at higher dosage of gamma radiation.

Example 2

In the second example, some of the formulations of example-1 were repeated. Here the base resin chosen was a random copolymer polypropylene, having melt flow rate of 25 gm/10min. The formulations (A2-C2) are given in Table-3. Sample B2 contained modifier ENGAGE® 8200 @ 2.5%, and sample C2 contained a linear low density polyethylene available from Huntsman Polymers Corporation of Odessa, Texas under the tradename of "LLDPE L8101", which is an octene copolymer. All these formulations were pre-blended with an un-stabilized random copolymer having MFR ~ 25 g/10min, and then were compounded by a 2.5" Davis Standard single screw extruder at a processing temperature (210°C). The test specimens (prepared - as described in example-1) were irradiated at 2.5 and 5.0 mrads of gamma radiation by Isomedix, Whippany, NJ. All these samples were tested as described in example 1.

The yellowness indices of these formulations had very minimal increase at 5 mrads of exposure vs. those of non-radiated samples, showing excellent color stability. Samples C2 had relatively lower increase in MFR at 5.0 mrads. This could be attributed to the presence of a LLDPE (L8101 @ 5 wt%) resulting in crosslinking. Addition of impact modifier such as ENGAGE® 8200 (even @ 2.5%) resulted in better impact energy than the control sample. Addition of L8101 @ 5 wt% did not provide much improvements in impact resistance.

Table 3

Sample ID	A2	B2	C2
PP Powder	99.55	97.05	94.55
CHIMASORB 944	0.15	0.15	0.15
GENOX EP	0.05	0.05	0.05
Ca stearate	0.05	0.05	0.05
DHT-4A	0.025	0.025	0.025
ENGAGE 8200	-	2.5	-
NA-21	0.175	0.175	0.175
L8101	-	-	5
Physical Properties of Samples from above at 0 megarads			
Sample	A2	B2	C2
MFR (g/10 min.)	26.8	26.9	23.8
% strain @ yield	13.8	14.2	14
Stress @ yield (psi)	4010	3800	3830
% strain @ break	650	640	370
Stress @ Break (psi)	2590	2500	2490
% haze 25mil	9.8	12.1	20.5
% haze 50mil	27.9	33.5	44.1
yellowness index	- 0.11	- 2.4	- 1.44
multi-axial impact @ 23°C, in-lbs	60	121	66
at 2.5 megarads			
MFR (g/10min)	127	134	117
%strain@yield	13.9	14.7	14.2
stress@yield, psi	4020	3810	3830
%strain@break	480	640	370
stress @ break (psi)	2480	2480	2490
% haze - 25 mil	9.9	12.1	20.5
% haze - 50 mil	28	33.2	44.3
yellowness index	0.72	- 1.25	0.38
multi-axial impact @23°C, in-lbs	52	91	42
at 5.0 megarads			
MFR (g/10min)	365	339	230
%strain@yield	14.4	15	15
stress @ yield, psi	3990	3810	3810
% strain @break	360	460	590
stress@break (psi)	2380	2370	2410
% haze - 25 mil	10	12.3	20.6
% haze - 50 mil	27.8	33.6	44.3
yellowness index	1.29	0.49	0.75
multi-axial impact @23°C, in-lbs	20	54	26

Example 3

In this example, we have repeated some formulations as given in example 1 and also included FS410 as a primary stabilizer system (see Samples F3 and G3). The control formulation was sample D3. The additive formulations (shown in Table-4) with an un-stabilized polypropylene powder having initial MFR ~ 25 dg/min were pre-blended and compounded by Haake TW100 twin screw extruder. The test specimens were irradiated at 2.5 and 5.0 mrads as done previously. The test specimens were tested as described in prior example 1.

The control sample D3 had YI colors of -1.79 (@ 0.0 mrads), 5.39(@2.5 mrads), and 5.91 (@5.0 mrads). The samples B3 (containing CHIMASSORB® 944 and GENOX® EP along with ENGAGE® 8200) had the least YI value of -1.67 after being exposed to 5 mrads of gamma radiation. Also the samples (F3 and G3) containing FS410 exhibited much lower YI (1.09 and 0.54 respectively) at 5 mrads' exposure. Hence, it is apparent that additive formulations consisting of either a combination of amine oxide and a HALS (i.e., CHIMASSORB® 994) or FS410 exhibited excellent color stability after being exposed to gamma radiation up to 5 mrads.

Table 4							
Sample ID	A3	B3	C3	D3	E3	F3	G3
PP Powder	99.625	94.625	99.475	94.23	99.575	99.575	99.625
CHIMASORB 944	0.15	0.15	0.15	-	0.15	-	-
GENOX EP	0.05	0.05	0.05	-	0.05	-	-
FS 410	-	-	-	-	-	0.2	0.2
Ca stearate	0.05	0.05	0.05	0.1	0.05	0.05	0.05
DHT-4A	0.025	0.025	0.025	0.05	0.025	0.025	0.025
HPN-68	0.1	0.1	-	-	0.05	0.05	0.1
Millad 3988	-	-	-	0.25	-	-	-
NA-21	-	-	-	-	0.1	0.1	-
ENGAGE 8200	-	5	-	-	-	-	-
TINUVIN 622 LD	-	-	-	0.2	-	-	-
NAUGARD XL-1	-	-	-	0.07	-	-	-
WESTON 619	-	-	-	0.1	-	-	-
LL-1002.09	-	-	-	-	5	-	-
Physical Properties of Samples from above							
at 0 megarads							
Sample	A3	B3	C3	D3	E3	F3	G3
MFR (g/10 min)	29	28	30	27	30	30	31
crystallization temp (°C)	125.8	125.1	121.9	122.3	125.8	125.1	121.9
% strain @ yield	13	14.3	13.7	12	14.1	13.9	12.9
Stress @ yield (psi)	4300	3890	4540	4440	4270	4240	4380
% strain @ break	630	440	730	370	720	770	690
Stress @ Break (psi)	2670	2560	2790	2650	2680	2770	2850
multiaxial impact @ 23°C, in-lbs	42	225	29	80	61	40	29
yellowness index	- 0.98	- 3.67	0.36	- 1.79	- 0/34	0	- 0.73
% haze 25 mil	10.7	15.2	5.8	16.8	8.9	9.2	11.4
%haze 50 mil	24.7	35.8	13.6	32.8	22.4	23	24.3
at 2.5 megarads							
MFR (g/10min)	127	123	129	152	129	112	107
crystallization temp (°C)	125.7	125.4	121.7	122.7	123.8	122.8	125.6
%strain@yield	13.4	14.3	13.6	11.9	13.8	13.2	12.6
stress@yield, psi	4280	3830	4540	4470	4270	4340	4350
%strain@break	200	300	460	320	610	600	610
stress@break (psi)	2500	2470	2650	2550	2570	2540	2540
multiaxial impact @23°C, in-lbs	26	77	22	32	33	30	30
yellowness index	- 0.13	- 2.15	1.24	5.39	0.57	0.46	- 0.27
at 5.0 megarads							
MFR (g/10min)	223	221	234	321	228	225	242
crystallization temp (°C)	125.4	124.9	121.8	121.2	123.1	121.6	124.9
%strain@yield	12.6	14.1	13.5	11.7	13.9	13.7	13.5
stress@yield, psi	4400	3820	4540	4460	4270	4250	4240
%strain@break	520	320	240	340	210	200	190
stress@break (psi)	2540	2440	2560	2540	2420	2450	2470
multiaxial impact @ 23°C, in-lbs	16	50	16	24	24	21	28
yellowness index	0.38	- 1.67	1.77	5.91	1.09	1.09	0.54

Example 4

In this example, we have repeated some formulations as given in example 1 using a polypropylene copolymer having MFR ~ 10 dg/min and also included FS410 as a primary stabilizer system (see Sample F4 in Table 4). The additive formulations with un-stabilized polypropylene powder having initial MFR ~ 10 dg/min were pre-blended and compounded by Haake TW100 twin screw extruder. The test specimens were irradiated at 2.5 and 5.0 mrads of gamma radiation as done previously. The test specimens were tested as described in prior example 1.

The properties of these formulations (sample A4 - F4) are given in Table 5. The sample B4 (containing CHIMASSORB® 944/GENOX® EP plus NA-21) had YI of 0.47 units (@ 0.0 mrads), 1.3 units (@2.5 mrads) and 1.76 units at (@5.0 mrads). Sample F4 (containing FS410 and NA-21) had the corresponding YI of 1.34, 2.44 and 2.52 units. Thus it is again evident that CHIMASSORB® 944 with either GENOX® EP (amine oxide) or FS042 (a hydroxyl amine) provided excellent color stability at 5 mrads of gamma radiation. Also, addition of MILLAD® 3988 (a sorbitol based nucleator/clarifier in sample C4) showed slight increase in YI compared to other samples (i.e., sample A4 with HPN-68, Sample B4 with NA-21). Note that the specific concentrations of nucleators/clarifiers were chosen, because they are known to improve clarity/nucleation at these levels. It was also evident that addition of 10% ENGAGE ® 8200 (i.e., sample D4) resulted in higher multiaxial energy, compared to other formulations.

Table - 5

Sample ID	A4	B4	C4	D4	E4	F4
PP Powder MFR 9dg/min.	99.625	99.575	99.55	89.525	99.5	99.575
Chimassorb 944,wt%	0.15	0.15	0.15	0.15	0.15	-
Genox EP,wt%	0.05	0.05	0.05	0.05	0.05	-
FS410,wt%	-	-	-	-	-	0.2
Calcium Stearate,wt%	0.05	0.05	0.05	0.05	0.05	0.05
HPN-68,%	0.125	-	-	0.075	0.1	-
NA-21,wt%	-	0.175	-	-	-	0.175
Millad 3988,wt%	-	-	0.2	0.15	0.15	-
Engage 8200,wt%	-	-	-	10%	-	-
Physical Properties						
at 0 Mrads						
MFR (g/10min)	11	11	11	12	11	11
%Strain @ Yield	13.3	14.3	14.4	16.6	13.9	14.3
Stress @ Yield,psi	3990	4060	4110	3360	4240	4240
%Strain @ Break	670	660	620	830	660	650
Stress @Break, psi	2650	2680	2700	2500	2710	2710
Multi-axial Impact @23°C, (in-lbs)	117	346	190	319	140	96
Yellowness Index	0.47	0.5	1.52	-1.65	1.13	1.34
%Haze - 25 mil	24.7	7.9	5.4	19.5	11.5	6.3
%Haze - 50 mil	47.4	19.4	10.6	46.2	23.5	13.1
at 2.5 Mrads						
MFR (g/10min)	63	66	71	56	55	54
% Strain @ Yield	12.7	13.9	14.8	16.6	14.3	14.3
Stress @Yield, psi	4050	4150	4040	3370	4040	4170
%Strain @ Break	610	580	530	810	660	670
Stress @ Break, psi	2550	2600	2630	2430	2630	2620
Multiaxial Impact @ 23°C, in-lbs	81	215	136	311	80	82
Yellowness Index	1.3	1.52	2.55	0.69	2.35	2.44
at 5 Mrads						
MFR (g/10min)	72	115	95	99	103	103
%Strain @ Yield	13.56	14.3	14.3	16.1	13.8	14.8
Stress @ Yield, psi	3930	4040	4180	3520	4180	4080
%Strain @ Break	460	650	630	880	660	540
Stress at Break, psi	2540	2440	2560	2430	2580	2560
Multiaxial Impact @23°C, in-lbs	29	128	36	301	30	42
Yellowness Index	1.76	1.86	2.87	0.59	2.21	2.52

Consideration must be given to the fact that although this invention has been described and disclosed in relation to certain preferred embodiments, obvious

equivalent modifications and alterations thereof will become apparent to one of ordinary skill in this art upon reading and understanding this specification and the claims appended hereto. The present disclosure includes the subject matter defined by any combination of any one of the various claims appended hereto with any one or more of the remaining claims, including the incorporation of the features and/or limitations of any dependent claim, singly or in combination with features and/or limitations of any one or more of the other dependent claims, with features and/or limitations of any one or more of the independent claims, with the remaining dependent claims in their original text being read and applied to any independent claim so modified. This also includes combination of the features and/or limitations of one or more of the independent claims with the features and/or limitations of another independent claim to arrive at a modified independent claim, with the remaining dependent claims in their original text being read and applied to any independent claim so modified. Accordingly, the presently disclosed invention is intended to cover all such modifications and alterations, and is limited only by the scope of the claims which follow, in view of the foregoing and other contents of this specification.